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ACCELERATED IMPLEMENTATION OF HARBOR PROCESSES RESEARCH

by

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BACKGROUND

Remedial investigations (RI) of Navy sediment typically involve sampling strategies based on those used at shore side groundwater sites and on the paradigms derived from those investigations. The most damaging to the Navy, and the least scientifically based, are those that relate sediment contaminants to historic shore side releases into waterways without some measure of contaminant transport. In addition to these problems, there is dearth of microbiological methods for collecting lines of evidence for intrinsic bioremediation despite the near universal acceptance of the ecological importance of such processes. Current evaluations of biological processes rely almost entirely on geochemical and analytical chemical inference of such rates, despite large variance in the intended time scales of geochemical measurements (months, years, decades) verses those known to change on microbiological time scales (minutes, hours). These critical methodological shortfalls result in Navy remedial project managers (RPMs) having to abandon any scientifically defensible attempt to estimate rates of intrinsic bioremediation. As a result, it is nearly impossible to scientifically validate any conceptual model involving the transport of organic contaminants to a Navy site and their subsequent biodegradation by natural bacteria. This would not be such a significant issue if it were technically and fiscally expedient to track the flux or determine a mass balance for a contaminant through Navy sediments.

Various lines of evidence are being developed through Office of Naval Research (ONR)-supported programs and are currently used at Navy field sites. Normally, these lines of evidence would be considered too “researchy” for inclusion in site evaluations. Considering the lack of counter evidence supplied by the regulators and stakeholders and the large stakes involved in the RIs, bioprocess and transport information may provide the most responsible and scientifically defensible use of taxpayer money. These lines of evidence will be presented as part of an oceanographic sampling strategy to directly compare contaminant biodegradation rates across a watershed. Stations were selected from Rapid Sediment Characterization (SPAWAR Systems Center (SSC)) and data from seven previous cruises in the lower Chesapeake Bay and its tributaries (Naval Research Laboratory (NRL)). Taken alone, a single line of evidence is as uninterpretable as ambient contaminant concentrations in the sediment; therefore, we present a strategy for coupling the lines of evidence of biodegradation with estimates of contaminant transport and measurement of watershed contaminants outside of the Navy study area (background or reference). Historical adversity to measuring contaminant concentration at more than a few sites (reference or background) outside of the Navy fence line has diminished our understanding of watershed background levels and sources. The strategy presented here ignores traditional boundaries in RI sample collection and provides a more ecologically relevant understanding of Navy sediments in the context of industrialized watersheds.

At many submerged, tidally influenced Navy sites, the primary evidence linking Naval operations to the contaminant levels are anecdotal reports of historical releases and lists of contaminants collocated in the adjacent shore side facility. The traditional strategies have also over relied on single, intensive sampling events, while ignoring processes that cause seasonal changes in ambient contaminant concentration. Understanding the magnitude of seasonal change alone can render comparison with ERL and ERM values irrelevant. Although this document is not intended to encompass all methods for measuring and interpreting contaminant sources to sediments, bioprocesses must be put in context of other transport and transformation rates as well as a sampling strategy to be useful to RPMs. Brief descriptions of the specific methods used in this study will be presented and put in context of the oceanographic sampling strategy as well as, suggestions on where these methods may apply to Chief of Naval Operations policy.

METHODS

PCA Analyses of Compound Ratios

One method for identifying or ruling out potential sources of organic contaminants to sediments involves analytical chemical measurement followed by Principle Component Analyses (PCA) of the ratios of individual compounds within the mixture. Much of the Y0817 and ONR supported work focuses on polycyclic aromatic hydrocarbons (PAHs) but this method can also apply to PCBs. Various sources of organic contaminants have distinct ratios of certain compounds and these ratios can be maintained with deposition into sediment. The strategy may be most effective for comparing sediments with high PAH levels and similar organic matter composition. An advantage of this analysis is that it can be performed on data that has already been collected as part of a typical Navy RI.

Compound Specific Stable Isotope Fingerprinting

An additional strategy for contaminant source identification among mixtures of organic compounds involves compound specific stable isotope fingerprinting. This method has been recently developed for PAHs and TNT in sediments under Y0817 and ONR. In addition to measuring the ambient concentration of individual compounds, the ratio of ^{13}C::^{12}C for each compound is determined. These ratios can be specific to the isolation of synthesis method or geographic origins of the source material and they are often preserved despite biological, chemical or physical processes acting on the compounds once released into the environment. This analysis is more expensive than standard concentration measurements for sediment but it can provide much higher resolution than less equivocal source determinations. It is also less sensitive to differences in organic matter concentrations that can change extraction efficiency between samples.

Rapid Characterization of PAHs and PCBs

Several of the lines of evidence of intrinsic bioremediation involve relatively large sample volume and need to be performed on sediment over a large range of PAH or PCB concentrations. With standard analytical chemical analysis, the investigator would not know the ambient contaminant concentration for several weeks after the sampling event. Rapid characterization techniques were used to estimate PAH and PCB concentration during the initial survey and then, the following day, selected stations were resampled for the more detailed genetic and biochemical analyses. The rapid characterization immunoassays can be performed in less than 24 hours, which allows it to be used in conjunction with a 2-day watershed sampling event.

Watershed Sampling Strategy

Navy sediment RIs typically involve a sampling strategy based on that used for investigation of shore side groundwater sites. Almost all of the samples are taken within the Navy fenceline along with one of two reference or background samples from outside the Navy site. This strategy is a result of NAVFAC directives against ecosystem level studies and sampling outside of the fenceline. In addition, economic concerns lead to a reduction in the total number of samples and sampling events. The complexities of the aquatic ecosystems and especially the importance of contaminant transport render the current strategy inadequate in providing a scientifically defensible understanding of the Navy's role in sediment contamination. Since 1997, NRL has been testing a different strategy for selection of stations and the number of sampling events that is based on an oceanographic understanding of the processes that are likely to play a role in the specific estuary that is being studied. These considerations include hydrodynamic issues based on water flow and physical characteristics of the area surrounding the Navy sediment site; importance of seasonal fluctuations in temperature and rainfall (e.g. tropical verses temperate); and, more evenly distributing sampling stations across the watershed. This strategy was applied during these sampling events in the lower Chesapeake Bay, as well as to investigations in Charleston Harbor, San Francisco Bay, and the upper Delaware and Schuylkill Rivers near Philadelphia. More information is available on the Philadelphia study as journal articles (Pohlman et al. 2002) and technical reports (Boyd et al. 1999) and the Charleston study will be published within the next year (Montgomery et al. 2003).

Seasonal Sampling Strategy for Contaminant Input and Reference Material (sediment traps, seston, nepheloid layer)

Navy sediment RIs focus on an individual survey of sediment and/or surface water stations. If subsequent samplings show lower contaminant concentrations, it is assumed to be due to heterogeneity in the sediments. In contrast, oceanographic-based sampling strategies provide quantitative information on the amount of variation that is due to normal seasonal changes in input and biotransformation. The two primary features of this proposed strategy involve repeatedly sampling the same watershed stations over several seasons and sampling organic contaminants bound to water column particles. Sampling the watershed three times annually for several years allows one to assign ecologically relevant error bars to the measured contaminant concentration at a site. The seasonal error is generally several orders of magnitude greater than the analytical error normally used for determining contaminant mass at a site. In addition, it can be important to measure the amount of contaminants bound to particles in the water column (seston), moving over the sediment tidally (nepheloid, or bottom boundary layer), or depositing onto the surface sediments (sediment traps). These parameters can be measured as part of the sediment survey and used to bound the seasonal variation in the sediment. For instance, in several Navy relevant ecosystems, PAH concentrations in the sediment traps were 10 to 15 times higher (based on dry weight) than in the surface sediments. The sediment trap material may provide a more site-specific and ecologically-relevant reference material than those "pristine" areas that are often chosen as reference sites in Navy RIs and can be performed within the same constraints of a typical RI investigation These measures can also be coupled with data on water flow to estimate contaminant transport through a specific area of the watershed.

Organotolerance of Bacterial Assemblage

Although volatile organic contaminants (VOCs) are often not a regulatory issue in estuarine sediments, they are often associated with higher molecular weight organics at their source. These latter compounds can often impact the environment; so identifying the source of VOCs to sediment may lead to identification of non-Navy PRPs that contribute the higher molecular weight organics to Navy sediments. Because of the episodic nature of industrial releases of VOCs to surface waters and sediments, it is difficult to determine if the areas of the ecosystem are being exposed to VOC release from other PRPs. One strategy for overcoming this is to employ a radiotracer assay that measures the response of the bacterial assemblage to VOC exposure. As bacteria in the sediment are repeatedly exposed to VOCs, many of them become organotolerant. The degree of organotolerance can be directly measured by exposing subsamples of the natural assemblage to increasing amounts of a VOC (e.g., naphthalene). The growth rate of bacteria in sediments from chronically exposed areas was not affected by the naphthalene additions where as those from sediments in more pristine areas were dramatically affected. More information on this assay and its application to sediments at Charleston Harbor, San Diego Bay, and the Philadelphia area is available as a technical report (Montgomery, et al. 2003).

Lines of Evidence of Continued Natural Recovery

Genetic Analyses for PCB Degradation
Genetic Analyses for PAH Degradation
Presence of Metabolic Intermediates

Alternate Electron Acceptor Availability
Survey and Depth Profile of PAH Mineralization

Despite the widespread recognition of the importance of measuring intrinsic rates contaminant biodegradation, there are few microbiologically valid methods currently used in Navy RIs. Just as with the other components of the site investigation, no single method is likely to yield such unequivocal results that it can be used alone. The most compelling argument for evidence of intrinsic bioremediation will involve the convergent conclusions of several independent methods. The lines of evidence presented in this study fall into one of four categories: genetic capacity for biodegradation; presence of metabolic intermediates known to result from biodegradation; change in ambient contaminant concentration in response to electron acceptor availability; and, radiotracer (e.g., ^{14}C-PAHs) mineralization of by the natural bacterial assemblage. Determining whether or not the natural bacterial assemblage has the capacity for metabolizing PAHs and PCBs can be determined by direct extraction of the sediment sample and genetic characterization. The advantage of this strategy is that the assay measures the *in situ* community with little manipulation that can change the assemblage prior to evaluation. The disadvantage is that it provides no degradation rate estimate and the degrading bacteria may be present but not active. The second line of evidence involves quantifying the metabolic intermediates of contaminant degradation. The advantage is that the assay reflects *in situ* community activity, though the disadvantage is that the degradation rate measurements have to be inferred from ratios and are not directly measured. The third measure looks to see how biodegradation rate changes in response to the addition of a limiting electron acceptor. The advantage is that parent compound biodegradation rates are directly measured, but the disadvantage is that the assay is performed *ex situ*. The final method measures intrinsic biodegradation rates using radiotracer additions of the contaminant. The advantage is that actual transformation and turnover rates are measured that can then be compared with transport rates. The disadvantage is that the assay is *ex situ* and the rates may be influenced by conditions that are changed during the 24-hour incubation. The best strategy for identifying sediment sites that are undergoing intrinsic bioremediation is to determine that the genetic capacity exists, find *in situ* evidence that metabolism is occurring (e.g., presence of intermediates), and then estimate the *in situ* rate via radiotracer additions. The estimated degradation rate or contaminant turnover time should then be compared with contaminant transport rates (e.g., sediment trap data) and ambient contaminant concentration to determine if the biodegradation rate is ecologically feasible.

APPLICATION OF HARBOR PROCESSES METHODS TO NAVFAC

In February 2002, CNO released a policy of sediment site investigation and response action (5090 Ser N453E/2U589601) that may provide a framework for applying some or all of the methods and strategies described above. The policy statements are first summarized and then the specific statement to which the method may apply is listed in Table 1.

(1) All sources shall be identified to determine if the Navy is solely responsible for the contamination.

(2) All investigations shall primarily be linked to a specific Navy CERCLA/RCRA site.

(3) All sediment investigations and response actions shall be consistent with Navy polices on risk assessment and background chemical levels.

(4) Sediment cleanup goals shall be developed based on site-specific information and shall be risk-based.

(5) The Navy shall not clean up contamination from a non-Navy source where the Navy has not contributed to the risk in sediments. The Navy will not clean up a site before the source is contained. Any potential re-contamination by non-Navy sources shall be documented.

(6) A monitoring plan with exit strategies shall be developed before collecting the first monitoring sample.

Table 1. CNO policy listed seven statements describing the types of information that should be gathered during a sediment site investigation. The methods that best apply to each statement are denoted by an ‘X’.

Method	CNO Policy Statement					
	1	2	3	4	5	6
PCA Analyses	X				X	
Stable Isotopes Fingerprint	X				X	
Rapid Characterization		X			X	
Watershed Sampling			X			X
Seasonal Sampling & Source Input	X		X		X	X
Organotolerance		X				
Lines of Evidence for Intrinsic				X		X

SUMMARY AND CONCLUSIONS

Estuarine and marine sediment investigations should employ oceanographic sampling strategies and methods if they are to provide information that is ecologically relevant and useful in understanding relevance of contaminants on Navy property relative to the rest of the industrialized watershed. Though it is currently expedient to rely on intensive one-time samplings and analytical chemistry, this strategy is expensive given the amount of interpretation and support the RPM receives and often open-ended. The onus is on the RPM to either prove that Naval operations did not result in environmental impact or that the contaminant concentrations are ecologically irrelevant. The current state of toxicology and environmental forensics does not allow the RPM develop a strong case regardless of the actual facts. However, it is currently possible to compare the amount of contaminants in Navy sediments to those in the rest of the industrialized watershed, as well as, suspended in the overlying water column. It is also possible to develop lines of evidence to support intrinsic bioremediation and to measure the turnover rate of these contaminants in the sediment. Combining measures of transport and biodegradation with a seasonal and watershed-level sampling approach can provide the RPM with an ecological understanding of the error, source, and ecological relevance of the contaminants on Navy sites. Once this information is published in peer-reviewed journals, the RPM will likely be in an advantageous position given the paucity and lack of site specificity of the published data that is available for a counter argument.

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